

# Determining Dissolution, Precipitation and Nucleation Rate Laws in Natural Systems

A.E. Blum

*U. S. Geological Survey, Boulder, Colorado, aeblum@usgs.gov*

## 1 INTRODUCTION

Many chemical changes in hydrologic systems are the result of dissolution and precipitation reactions. There is a growing body of theoretical work describing the dissolution and precipitation process. However, the factors potentially controlling dissolution and precipitation are very diverse, and it is difficult to design definitive experiments that will accurately reproduce the hydrologic and chemical complexity of natural systems. In addition, geologic time scales may be very important in natural systems, and are impossible to duplicate experimentally. Consequently, there is difficulty in predicting rate laws for dissolution and precipitation reactions which can be incorporated in reaction-transport modeling.

## 2 SPARINGLY SOLUBLE SALTS (*mostly calcite*)

The behavior of sparingly soluble salts, the most important of which is calcite, appears to be similarly in experimental and natural systems. Thus, experimental determinations of dissolution and precipitation rates under the appropriate conditions, such as the rates of calcite precipitation determined by Plummer et al. (1978) are probably a reliable prediction of the kinetics of those processes in natural systems. Observations of the surface evolution and reaction mechanisms sparingly soluble salts seem consistent with the general theoretical approaches to crystal dissolution as growth. The details may not be clear, but the approach is insightful and significant. Commonly, the reaction rates of sparingly soluble salts are rapid enough that reaction-transport models may use the assumption of local equilibrium, and not introduce kinetics.

As always, there are notable cautions and exceptions. One of the most common examples is the severe inhibition of calcite dissolution by even trace amounts of dissolved phosphate Berner and Morse (1974). This was discovered by oceanographers trying to explain the depression of the calcite compensation depth in the oceans. Inhibiting effects have been investigated in several systems, but there are a nearly infinite combination of possible salts and inhibitors, and the possibility of inhibition must always be considered. The good news is that testing inhibition in the laboratory for a specific system is practical.

Another caveat is that composition of the solution can play a critical role in the kinetics of dissolution and precipitation reactions. For example, Plummer et al. (1992) experimentally measured the dissolution kinetics of aragonite-strontianite solid solutions  $[(\text{Ca,Sr})\text{CO}_3]$ . What they found is that the composition of the solid phase had no relationship to the dissolution rate. Rather, the dissolution kinetics was controlled by the rate of dissolution of the solid which predicted to be precipitated from the solution Ca/Sr ratio. What they believe was happening is that there is reversible dissolution and precipitation occurring at the surface, consistent with the theory of microscopy reversibility (that the net reaction rate is the difference between the forward and reverse reactions at the surface on a microscopic scale). Initially the

bulk crystal dissolves, but the composition of the precipitate in the back reaction is determined by composition of the solution. Within minutes, the crystal surfaces are completely covered by a thin layer reflecting the composition of the solution, and it is the solution composition which then controls the kinetics of any further dissolution.

## 2 DISSOLUTION OF ALUMINO-SILICATES

### 2.1 *Discrepancy between experimental and natural dissolution rates*

The feldspar minerals, particularly plagioclase, often dominate weathering in soils and watersheds, and have been the focus of a large proportion of both the experimental and field studies of aluminosilicate dissolution. There are difficulties and ambiguities in both laboratory and natural feldspar dissolution rates. However, it is now quite clear that there is a large discrepancy between experimentally measured dissolution rates of feldspars and dissolution rates of feldspars measured in the field, with the experimental rates  $10^2$  to  $10^5$  times faster than natural rates. This data has been most recently compiled by White and Brantley (2003). It appears that experimental dissolution rates of aluminosilicates have very little relevance to natural reaction rates, and use of the experimental rates in reaction transport models of natural systems is difficult to justify. As a consequence, research has shifted over the last ten years away from experimental weathering studies to field studies designed to examine the processes operating in natural systems.

There are systematic variations observed in weathering in soils. While absolute experimental dissolution rates are far too fast, the relative dissolution rates of minerals in experimental and natural systems are roughly similar, with quartz < K-feldspar < plagioclase < amphiboles < pyroxenes < olivine. Elemental fluxes from watersheds also indicate systematic variations, with weathering rates increasing with increasing precipitation and higher temperatures (White and Blum, 1995; Oliva, et al., 2003).

### 2.2 *Controls on feldspar weathering rates in soils*

There is a lot of speculation, but only a rough outline of reasons for retardation of natural dissolution rates is emerging. An important observation is that most weathering occurs in the top few meters of regolith. Below the B soil horizon, there is much less change in the chemistry of soil solutions, and much less evidence of primary mineral alteration or clay formation. The near-surface is also the area of greatest biological activity. However, all the proposed effects of biota tend to increase weathering rates, and no plausible biotic mechanism for the retardation of weathering rates has been established.

The most likely mechanisms retarding feldspar dissolution rates in soils are: a) the interstitial soil solutions approach equilibrium with the feldspars, which halts further dissolution until the interstitial water is mobilized, and b) the most reactive portions of the mineral grains dissolve first, and the reactivity of the minerals decreases with the extent of weathering, and therefore roughly with age. Laboratory experiments simply cannot simulate the effects of geologic time on the reactivity of minerals.

There are several lines of evidence favoring the effect of the approach to equilibrium with feldspars. The effect of saturation state on feldspar dissolution has been observed experimentally, although the details of how the dissolution rate decreases as equilibrium

is approached remains uncertain (Burch et al., 1993; Oelkers et al., 1994). Soil hydrology is quite complex, and episodic wetting and drying events can mobilize and concentrate the soil solutions, and channeling and capillary tension make it difficult to quantify the flow paths of water through the soil matrix. Soil solutions can also only be sampled at times of high water content, and therefore the chemistry of the pore water is difficult to characterize accurately. If feldspars began reacting with rain water at laboratory rates, the water in a 2  $\mu\text{m}$  pore would be saturated with plagioclase within hours, and all further reaction would cease, suggesting that saturation within soil pores is likely. Soils are also the zone of major clay formation, meaning that soil pore solutions must be supersaturated with respect to clays for some period of time. Supersaturation with kaolinite or smectite almost requires saturation with respect to the feldspars. Finally, if soil water becomes saturated with respect to feldspars in the near surface, there will be little further reaction as the water is mobilized to greater depths, which is consistent with the major alteration in soils occurring only near the surface.

The work of White and Brantley (2003) also demonstrates a correlation between a decreasing weathering rate and increasing age of the substrate. Feldspars preferentially weather at defect sites, forming dramatic etching features which permeate the grains, and some sort of preferential weathering at defects obviously occurs. However, the age of the substrate alone can not explain the concentration of weathering at the soil surface, and therefore is probably not the complete story. If high solubility material at the soil surface is removed with time, the solution would react with material at greater depths, resulting in incomplete removal of minerals from the soil surface, and the propagation of the zone of rapid weathering downward, and this pattern is not observed. However, these mechanisms are not exclusive, and both approach to equilibrium, the reactivity of the substrate, as well as other mechanisms may operate simultaneously and to different extents in different environments.

### 2.3 *Feldspar weathering rates in aquifers*

Zhu et al. (in prep.) determined in situ feldspar dissolution rates along 15 flow paths within the Navajo sandstone aquifer at Black Mesa, Arizona, using the inverse mass balance calculation described in Zhu (2000). Calculated plagioclase and K-feldspar dissolution rates are  $10^{-16.2 \pm 0.4} \text{ mol m}^{-2} \text{ sec}^{-1}$  and  $10^{-18.1 \pm 0.3} \text{ mol m}^{-2} \text{ sec}^{-1}$ , respectively. These rates are five orders of magnitude slower than laboratory measured rates, and are among the slowest rates reported in natural systems. Calculations from published water chemistry from other aquifers suggest similar feldspar reaction rates.

The ground waters from Black Mesa are all close to equilibrium with K-feldspar and plagioclase, and approach to equilibrium is the most likely cause for retarded feldspar dissolution rates in the aquifers. However, approach to equilibrium is a necessary but not a sufficient condition; there must be another coupled mechanism that prevents groundwater reaching complete equilibrium with feldspars, and allows continued reaction down gradient at a slow but nearly constant rate. They suggest that the slow precipitation of clays (in the case of Black Mesa, smectite) is the rate limiting step for the overall weathering reaction in these groundwater aquifers. Clays form primarily in the soils, but the role of clay precipitation in limiting weathering in soils and other weathering environments is still quite uncertain. However, the precipitation rate of

clays is an area where there is very little data, but a process that may have an important role in the rate of overall reactions in some circumstances.

### 3 NUCLEATION AND CRYSTAL SIZE DISTRIBUTIONS

There is very little information on the nucleation and growth kinetics of many important minerals, particularly clays and oxides. However, crystal size distributions (CSD) record a history of the condition under which minerals nucleated and grew. Eberl et al. (1998) has observed that there are only five basic shapes of crystal size distributions observed in a wide range of geological environments. They have attempted to relate the CSD to the solution conditions during mineral formation. For example, an asymptotic distribution with many small particles is indicative of continuous nucleation and growth with supersaturation remaining sufficient to sustain nucleation. Ostwald ripening generates a very distinctive size distribution, and nucleation followed by growth with no further nucleation yields a log-normal size distribution. There are still a number of uncertainties in the growth laws that can generate and sustain CSD's, particularly log-normal distributions, but I believe that CSD's hold a large amount of information on reaction conditions during precipitation that is not currently being utilized by many geochemists.

### 4 CONCLUSIONS

Experimentally determined rate laws for sparingly soluble salts, such as calcite, can yield useful guidance for the rates used in reaction-transport models. However, the available data all suggest that the laboratory determined rates for the dissolution of feldspars and other aluminosilicates have little relation to the rates of these reactions in natural environments. Rather, it appears that unsaturated hydrology, approach to equilibrium and possibly the precipitation kinetics of secondary phases control the rates of natural feldspar dissolution, and most likely other aluminosilicates. Both experimental and natural data on nucleation and growth rates of minerals, particularly clays, are scarce. However, the crystal size distributions of the secondary phases can yield helpful information on chemical conditions under which the minerals formed.

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